

Paper VIII

VIII. Nonlinear Optical Properties of Open-Shell Polychlorotriphenylmethyl Radicals

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Polyhedron, (In press)

Paper IX

IX. A new Valence Tautomerism Example in an Electroactive Ferrocene Substituted Triphenylmethyl Radical

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J. Am. Chem. Soc. (In press)

Paper X

X. Supramolecular Photomagnetic Materials: Photoinduced Self-Assembly of Ferrocene-Based Polychlorotriphenylmethyl Radicals

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- [22] For example, we have developed related methodology starting out from “[Ru(H)(η⁵-2,4-dimethylpentadienyl)₂](BF₄)” (T. D. Newbound, L. Stahl, M. L. Ziegler, R. D. Ernst, *Organometallics* **1990**, *9*, 2962–2972); see the patents listed in footnote [9] in ref. [3]. After submission of this paper, we learned that parallel work is in print (A. Bauer, U. Englert, S. Geysler, F. Podewils, A. Salzer, *Organometallics* **2000**, *19*, 5471–5476).
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A New Photomagnetic Molecular System Based on Photoinduced Self-Assembly of Radicals**

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Dedicated to Professor Fred Wudl on the occasion of his 60th birthday

The synthesis and characterization of supramolecular magnetic materials based on the self-assembly of open-shell molecules are currently of great interest.^[1] The construction of such solids requires that the structural subunits exhibit noncovalent interactions that can be controlled in a predictable manner. The noncovalent intermolecular interactions that have been used to date for the assembly of such molecular subunits are hydrogen bonding,^[2] transition metal

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ligation,^[3] stack-type alignment,^[4] and bridging of ion radicals by their counterions.^[5] Among these interactions, hydrogen bonding has emerged as a particularly useful and efficient tool. Indeed, transmission of magnetic interactions through hydrogen bonds was first observed with transition metal complexes.^[6] Since then, several hydrogen-bonded organic magnets have been reported.^[2] However, to the best of our knowledge, hydrogen-bonded supramolecular magnetic materials whose properties may be systematically tuned and/or controlled by external stimuli have so far not been reported despite the enormous interest in switchable magnetic materials.

Light is a particularly efficient stimulus for inducing changes in the magnetic properties of a given material. In fact, examples of photomagnetism in inorganic magnetic systems and in covalently linked organic polyradicals have already been reported. For instance, Hashimoto et al. reported photoinduced magnetization changes in a cobalt–iron cyanide complex,^[7] which confirmed the possibility of modifying long-range magnetic ordering by photons. Furthermore, photoinduced magnetic changes in pure organic materials have also been described, for example, as in the photoisomerization of a carbene^[8] and in the spin isomerism of a non-Kekulé diradical.^[9] More recently, Irie and Matsuda described a photochromic system that interconverts reversibly between a singlet and a triplet high-spin ground state,^[10] and Iwamura et al. reported a diradical species bearing two stable nitroxide radicals connected through an isomerizable unit.^[11]

Herein we report a new photomagnetic system based on the photoinduced *trans*→*cis* isomerization of **1**. The *trans*-**1** isomer exists in solution as a monomeric species, whereas the *cis*-**1** isomer aggregates in solution through the formation of hydrogen bonds to give a thermodynamically stabilized diradical dimer with strong antiferromagnetic interactions. Although numerous photochromic supramolecular systems have been described up to now,^[12] this photoinduced self-assembly process represents the first example of a photomagnetic system based on a supramolecular phenomenon.

The ferrocenyl Schiff base polychlorotriphenylmethyl radical (**1**) was obtained by a condensation reaction between the (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical and ferrocene monocarboxaldehyde. Since the condensation reaction is not stereoselective, the *trans* and *cis* isomers of compound **1** were present in the reaction product. Both isomers, *trans*-**1** and *cis*-**1**, were isolated as stable species in solution and in the solid state, and were characterized by different techniques such as elemental analysis, matrix-assisted laser desorption time-of-flight (MALDI-TOF) mass spectrometry, HPLC, cyclic voltammetry, FT-IR, UV/Vis/NIR, and ESR spectroscopy.

Single crystals for the X-ray structure analysis of *trans*-**1** were grown by slow evaporation from a carbon tetrachloride/hexanes (1/1) mixture.^[13] The structure of *trans*-**1** (Figure 1; ORTEP view) reveals almost eclipsed cyclopentadienyl rings and a *trans* configuration at the CH=N double bond. Despite the available resonance pathway and the *trans* configuration, the η -C₃H₄ and the C₆H₂Cl₂ rings are twisted by an angle of about 28°. Presumably, the steric interactions between the hydrogen atom of the CH=N group one of the *ortho* hydrogen

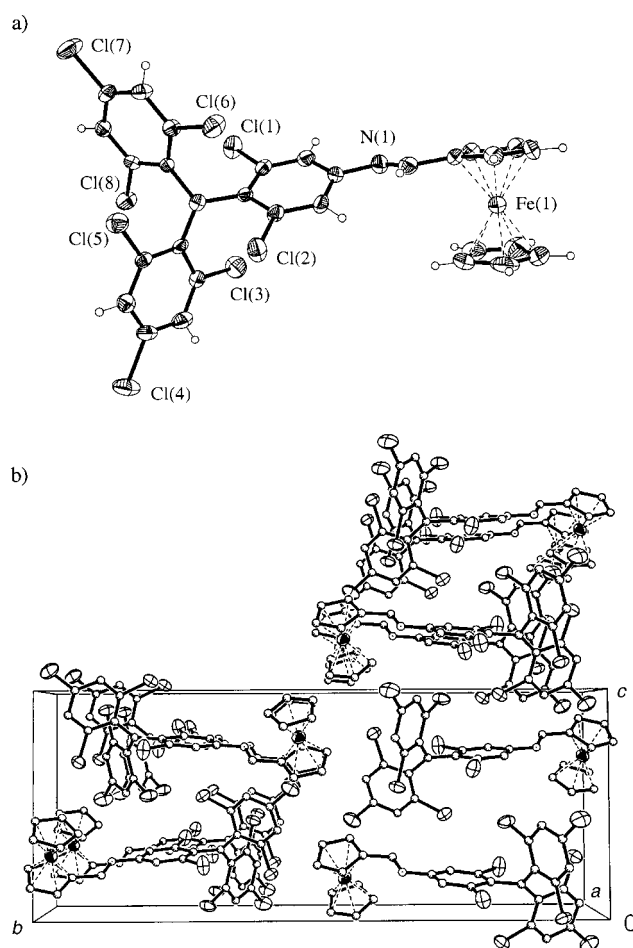
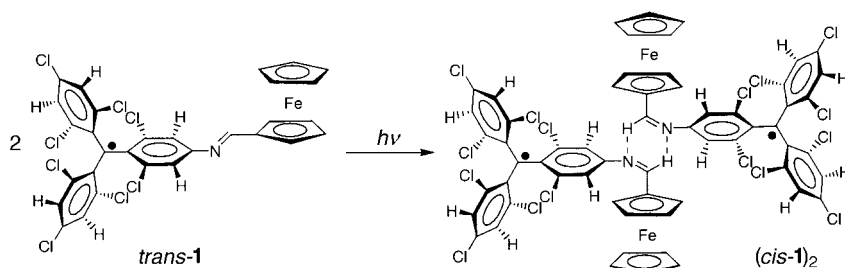


Figure 1. Molecular structure (with 50% ellipsoids; top) and crystal packing (bottom) of *trans*-**1**.

atoms of the benzene ring prevents a planar arrangement. The solid-state packing of *trans*-**1** is best described as enantiomerically related pairs of molecules (see Figure 1b). Stacking of these related pairs occurs with continuous staggering along the *c* axis and with a head-to-tail pairing along the *b* axis. The relative arrangement and the considerably large distances between neighboring molecules excludes the presence of hydrogen bonds among neighboring CH=N units. Under these circumstances, the largest driving forces for such molecular packing are dipole–dipole and van der Waals interactions, which lead to an efficient filling of space. Unfortunately, despite the use of different crystallization techniques, we have been unable to obtain crystals suitable for determining the X-ray structure of the *cis*-**1** isomer.^[14]

The cyclic voltammetric response of *trans*-**1** and *cis*-**1** show one reversible oxidation process at +0.61 and +0.72 V, respectively, and one reversible reduction process at –0.66 and –0.67 V, respectively (vs. a Ag/AgCl electrode in CH₂Cl₂). The reversible oxidation process arises, in both cases, from the oxidation of the iron atom of the ferrocene unit, while the reversible reduction process is associated with the reduction at the triphenylmethyl radical unit to the corresponding carbanion; as ascertained by UV/Vis and ESR spectroelectrochemical experiments. ESR spectroscopy provides more detailed and definitive information about the

molecular and electronic structure of both isomers in solution. Thus, the isotropic X-band ESR spectrum of the radical *trans*-**1** in toluene/dichloromethane (1/1; $c = 10^{-5} \text{ mol L}^{-1}$) at 220 K, is concentration-independent and shows the lines corresponding to the coupling of the unpaired electron with the different nuclei with nonzero magnetic moments; that is, with ^1H , ^{14}N , and naturally abundant ^{13}C isotopes at the α and aromatic positions. Computer simulation gave the isotropic g values (g_{iso}) and the isotropic hyperfine coupling constants (a_i). The g_{iso} value is 2.0030, which is very close to the values for other polychlorotriphenylmethyl radicals.^[15] The values of the coupling constants of *trans*-**1** are: $a(^{14}\text{N}) = 1.18 \text{ G}$; $a(^1\text{H}_{\text{meta}}) = 1.06 \text{ G}$; $a(^1\text{H}_{\text{trans}}) = 0.25 \text{ G}$; $a(^{13}\text{C}_{\alpha}) = 28.5 \text{ G}$; $a(^{13}\text{C}_{\text{bridge}}) = 12.5 \text{ G}$; $a(^{13}\text{C}_{\text{ortho}}) = 10.3 \text{ G}$.^[16] At 160 K, its spectrum shows a single broad line characteristic of an isolated free radical in a rigid medium with a low magnetic anisotropy. This fact clearly shows that the *trans*-**1** isomer exists in solution as a monomeric species. Surprisingly, the X-band ESR spectrum of the *cis*-**1** radical in toluene/dichloromethane (1/1) at 220 K did not show the lines corresponding to the coupling of the unpaired electron with the different magnetic nuclei, but the characteristic fine structure of a triplet species. The zero-field splitting parameters obtained by computer simulation of the spectra obtained at 160 K are $|D'| = 25.2 \text{ G}$ and $|E'| = 0$. This behavior has been attributed to the formation of a dimeric species which is held together by intermolecular C-H...N hydrogen bonds between the CH=N groups of two different molecules (Scheme 1). Semiempirical ZINDO/1 calculations^[17] revealed that the H-bonded dimeric form of *cis*-**1** corresponds to an energy minimum, while for the *trans*-**1** isomer similar H-bonded dimeric or polymeric species



Scheme 1. Photoinduced *trans* \rightarrow *cis* isomerization of **1**.

do not correspond to energy minima; probably because of the steric hindrance developed in such species. These calculations also revealed that the dimeric species (*cis*-**1**)₂ are more stable than the monomeric species *trans*-**1** by 7 kcal mol⁻¹. The forbidden $\Delta m_s = \pm 2$ transition characteristic of triplet species was also observed at the half-field region of the spectrum of *cis*-**1** and the intensity of the corresponding signal (I_{pp}), obtained by double integration, was measured in the 4–100 K temperature range. Since the experimental value of $I_{\text{pp}}T$ is proportional to the population in the triplet state, the fact that $I_{\text{pp}}T$ decreases with decreasing temperature indicates that the ground state of the dimeric species is the singlet state and the triplet state should be associated with a thermally accessible excited state. A separation of $54 \pm 2 \text{ K}$ (38 cm^{-1}) between

both states was obtained from the fitting of the experimental data to a Bleaney–Bowers equation.^[18]

Our interest in compound **1** was considerably enhanced when it was found that the ESR spectrum of *trans*-**1** in methylcyclohexane exhibited a time dependence behavior under in situ irradiation at 415 nm,^[19] a result that is consistent with the conversion from the *trans*-**1** to the *cis*-**1** isomer (Figure 2). After eight hours of irradiation a mixture with a

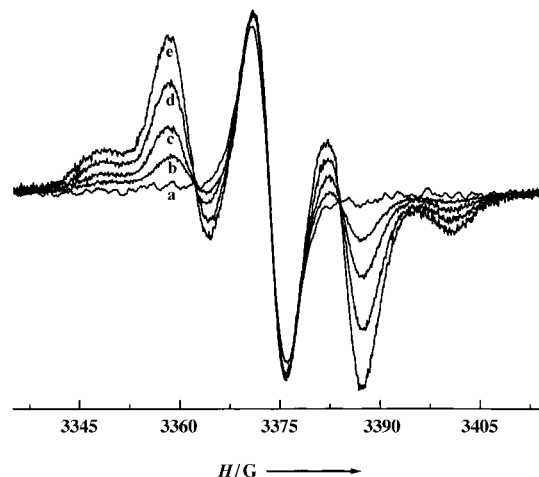
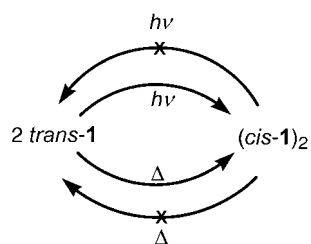


Figure 2. Photoinduced *trans* \rightarrow *cis* isomerization of **1** monitored by ESR spectroscopy. $t = 0$ (a), 1 (b), 3 (c), 5 (d), 8 h (e).

cis:trans ratio $\geq 90:10$ was obtained; as confirmed by computer simulation. The photoinduced *trans*-**1** \rightarrow *cis*-**1** isomerization in methylcyclohexane at room temperature was also monitored by UV/Vis spectroscopy. Indeed, the *trans*-**1** and

cis-**1** isomers show characteristic UV/Vis absorption bands for the radical (377 nm) and conjugated ferrocene (408 nm) chromophores. The main difference lies in the relative intensity of both bands. The band at 377 nm for the *trans*-**1** isomer is less pronounced, whereas that at 408 nm is more intense than the corresponding bands for the *cis*-**1** isomer. This fact allowed us to study the effect of irradiation upon a solution of *trans*-**1** in methylcyclohexane by UV/Vis spectroscopy. The in situ irradiation of *trans*-**1** ($c = 10^{-5} \text{ mol L}^{-1}$ in methylcyclohexane) was carried out using 415 nm

light in a quartz cell at room temperature for 2 h. During the irradiation of the *trans*-**1** solution, the absorption band at 377 nm increases, whereas the absorption band at 408 nm decreases; an isosbestic point occurs at 382 nm. This confirms a neat transformation from the *trans*-**1** to the *cis*-**1** isomer. Finally, it must be emphasized that irradiation of a *cis*-**1** solution ($c = 10^{-5} \text{ mol L}^{-1}$) did not indicate the presence of the reverse photoisomerization process, either by ESR and/or by UV/Vis spectroscopy. Moreover, warming *cis*-**1** solutions in three different solvents (methylcyclohexane, toluene, and acetonitrile) up to 80 °C provided no evidence of a thermally induced backward *cis*-**1** \rightarrow *trans*-**1** isomerization, while the *trans*-**1** \rightarrow *cis*-**1** isomerization process takes place in the three studied solvents (Scheme 2).



Scheme 2. Overview of the photochemically and thermally possible isomerizations of **1**.

In summary, the photoinduced *trans* → *cis* isomerization of **1** has been monitored by UV/Vis and ESR spectroscopy. Interestingly, the *cis*-**1** isomer aggregates in solution at low temperatures through the formation of hydrogen bonds to give thermodynamically stable diradical dimers with strong antiferromagnetic interactions. This one-way photoinduced self-assembly process represents an interesting example of a photomagnetic system based on a supramolecular phenomenon in which a doublet species is converted into a singlet one.

Experimental Section

1: To a dry solution of (4-amino-2,6-dichlorophenyl)bis(2,4,6-trichlorophenyl)methyl radical in toluene, which was obtained as previously described,^[20] was added ferrocene monocarboxaldehyde in the presence of molecular sieves. The mixture was heated up to 60 °C and stirred for 48 h. After removal of the molecular sieves and evaporation of the solvent, a brown precipitate was obtained, which contained a mixture of *cis*- and *trans*-**1**. The *trans*-**1** isomer was isolated as a dark brown microcrystalline material by recrystallization from *n*-hexane, and the *cis*-**1** isomer was isolated as a dark green powder by flash chromatography (Florisil (magnesium silicate), carbon tetrachloride). *trans*-**1**: elemental analysis (%): calcd for C₃₀H₁₆Cl₈NFe: C 49.4, H 2.21, N 1.90; found: C 49.6, H 1.8, N 2.1; IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3420, 2967, 2913, 1631, 1556, 1536, 1465, 1371, 1261, 1225, 1182, 1137, 1104, 1021, 858, 809 cm⁻¹; UV/Vis (methylcyclohexane): $\lambda(\epsilon)$ = 377 (20300), 409 (14900), 565 nm (1863). *cis*-**1**: elemental analysis (%): calcd for C₃₀H₁₆Cl₈NFe: C 49.4, H 2.21, N 1.90; found: C 49.8, H 2.0, N 2.2; IR (KBr): $\tilde{\nu}_{\text{max}}$ = 3434, 2925, 2849, 1715, 1631, 1552, 1526, 1487, 1383, 1371, 1292, 1227, 1182, 1134, 1076, 1057, 926, 858, 817, 788 cm⁻¹; UV/Vis (methylcyclohexane): $\lambda(\epsilon)$ = 377 (23300), 407 (13600), 578 nm (2940).

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Formation of a biradical species from a monoradical with a photo- and thermo isomerizable imine group

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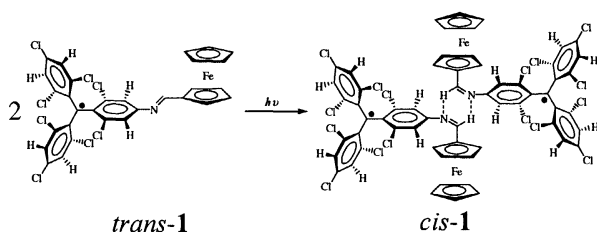
Abstract

The thermally induced *trans*-1/*cis*-1 isomerization process is studied here. The *trans*-1 → *cis*-1 isomerization takes place in three solvents with different polarities whereas *cis*-1 did not evidence the presence of a backward *cis*-1 → *trans*-1 isomerization, independently of the polarity of the solvent used. This fact revealed that the *cis*-1 isomer is thermodynamically more stable probably due to the formation of a hydrogen bonded biradical species, as confirmed by ZINDO/1 semiempirical calculations.

Keywords: triphenylmethyl radical, *cis*-*trans* isomerization, biradical, photomagnetism

1. Introduction

In a previous communication,¹ we reported the synthesis and characterization of the ferrocenyl Schiff-base polychlorotriphenylmethyl radical (**1**), which exhibits a photoinduced *trans*-1 to *cis*-1 photoisomerization. The *cis*-1 isomer aggregates in solution, as confirmed by ESR experiments, originating a hydrogen-bonded diradical species in which strong antiferromagnetic interactions are developed. This fact was used to establish for the first time a photomagnetic supramolecular assembly.²



Here we report a more detailed study of the relative stability of both isomeric forms. We will show, either experimentally and theoretically, that this represents a case of a one-way isomerization process,³ since the *cis*-1 isomer is thermodynamically stabilized by the formation of the hydrogen bonded dimeric species.

2.- Experimental

Compounds *trans*-1 and *cis*-1 were obtained as previously described.¹ HPLC chromatograms were obtained using octadecyl polysiloxane (ODS) as the stationary phase and a mixture of acetonitrile and THF (70:30) as the mobile phase. The geometry of *trans*-1 and *cis*-1 were minimized using ZINDO-1 semiempirical minimizations.⁴ In each case, different initial input conformations differing by the rotation angle around the single bond that connects the phenylene and cyclopentadienyl rings with the imine bridge, were used. Independently of the input model used, the minimized geometries converged in similar close-lying minima.

3. Thermally induced *trans*/*cis* isomerization

In our previous communication we showed that the ESR spectrum of *trans*-1 exhibited a time dependence behavior under “*in-situ*” irradiation, consistent with the interconversion from the *trans*-1 to the *cis*-1 isomer. The photoinduced *trans*-1 to *cis*-1 isomerization was also monitored by UV-vis spectroscopy. On the contrary, irradiation of a *cis*-1 solution did not evidence the presence of photoisomerization processes, either by ESR or UV-vis spectroscopy.

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Here we present new studies of the thermally induced *trans*-1 \rightarrow *cis*-1 isomerization. Such studies were carried out in three solvents with different polarities (methycyclohexane, toluene and acetonitrile). Initially, a degassed solution of *trans*-1 was warmed up to 80°C and its evolution followed with the time by HPLC chromatography and UV-vis spectroscopy. The experimental results confirmed that independently of the solvent used and in absence of light irradiation, the thermally induced *trans*-1 \rightarrow *cis*-1 isomerization takes place. As an example, the time-dependence of an acetonitrile solution of *trans*-1 ($c = 1.10^{-5} \text{ mol.l}^{-1}$) at 80 °C is shown in Figure 1. The initial chromatogram shows the characteristic peak of the *trans*-1 isomer. In the second chromatogram, obtained approximately one hour after, the intensity of the peak characteristic of the *trans*-1 form decreases whereas the intensity of the peak characteristic of the *cis*-1 isomer, which appears at lower retention times, increases. Such tendency is continued and after five hours, a mixture with a *cis:trans* ratio $\geq 95:5$ is attained. We have also examined the thermal behavior of *cis*-1 in the same three above-mentioned solvents. In all the cases there was no evidence of a thermally induced backward *cis*-1 \rightarrow *trans*-1 isomerization, neither by HPLC or UV-vis techniques. It is worth noting that at 20°C in degassed solution both isomers are stable in same conditions at least during five hours.

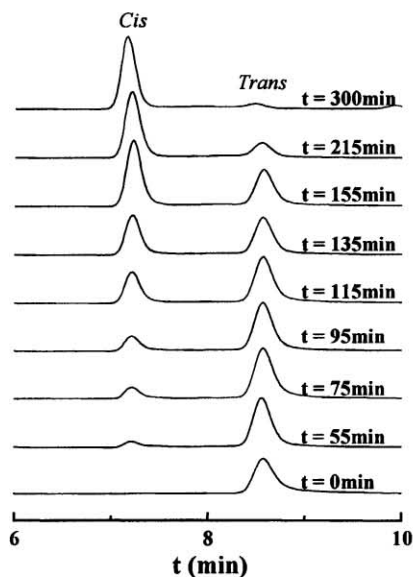


Fig. 1. Evolution of the interconversion of an acetonitrile solution of the isomer *Trans* at 80°C.

4. Theoretical studies

To assess the relative energy of the hydrogen bonded dimeric species of *cis*-1, ZINDO/1 semiempirical calculations were also performed.

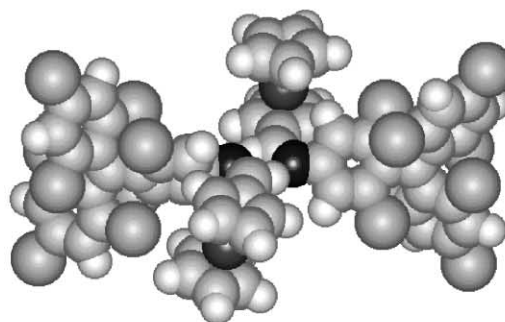


Fig. 2. ZINDO/1 minimized structure of the hydrogen bonded dimeric species of *cis*-1

These calculations revealed that the hydrogen bonded dimeric species of *cis*-1 (see Figure 2) corresponds to an energy minimum while for the *trans*-1 isomer, similar hydrogen bonded dimeric or polymeric species do not correspond to energy minima, probably because of the high steric hindrance developed. These calculations also revealed that the dimeric species of *cis*-1 are more stable than the monomeric species of *trans*-1 by 7 Kcal/mol.

5. Conclusions

In summary, the thermal *trans*-1 \rightarrow *cis*-1 isomerization has been obtained by UV-vis and HPLC chromatography in three solvents with different polarities at 80°C. On the contrary, a *cis*-1 solution did not evidence the presence of a backward *cis*-1 \rightarrow *trans*-1 isomerization at 80°C, independently of the polarity of the solvent used. At 20°C both isomers are stable. Such result revealed that the *cis*-1 isomer is thermodynamically more stable than the isomeric form *trans*-1, probably due to the formation of a hydrogen bonded diradical species. ZINDO/1 semiempirical calculations definitively confirmed the relative thermodynamical stability of both isomeric forms.

This work was supported by grant from DGES (project PB96-0802-C02-01), CIRIT (project SGR 96-00106) and the 3MD Network of the TMR program of the E.U. (contract ERBFMRX CT980181). D. R.-M. is grateful to the Generalitat de Catalunya for a postdoctoral grant and I. R. is grateful to a CSIC-Carburos Metálicos and ESF for a travel fellowship.

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EPR study of the *trans* and *cis* isomers of a ferrocenyl Schiff-based polychlorotriphenylmethyl radical

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Abstract

The isomeric *trans*-**1** and *cis*-**1** radicals have been studied by EPR spectroscopy. At 220 K, the EPR spectrum of the *trans*-**1** isomer shows a hyperfine structure corresponding to the coupling of the unpaired electron with the different nuclei with non-zero magnetic moments. In contrast, the EPR spectrum of the *cis*-**1** isomer at similar temperatures shows the characteristic structure of a triplet species. The differences in the EPR spectra of both isomers have been attributed to the fact that the *cis*-**1** isomer aggregates in solution originating the thermodynamically stabilized hydrogen-bonded diradical species, in which strong antiferromagnetic interactions are developed. EPR frozen solution experiments, down to liquid helium temperature, showed that the magnetic ground state of the resulting dimeric species is the singlet state and the triplet should be associated with a thermally accessible excited state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: *cis*; *trans*; Supramolecular; Hydrogen-bond; Diradical; EPR spectroscopy

1. Introduction

Obtaining hydrogen-bonded supramolecular magnetic materials whose properties may be systematically tuned and/or controlled by external stimuli remains an elusive field despite its enormous interest. Very recently [1] we reported the synthesis and characterization of the ferrocenyl Schiff-based polychlorotriphenylmethyl radical (**1**), which exhibits a photoinduced *trans*-**1** to *cis*-**1** isomerization (see Scheme 1). Interestingly, the *cis*-**1** isomer aggregates in solution originating the thermodynamically stabilized hydrogen-bonded diradical species, in which strong antiferromagnetic interactions are developed. This was the first example, so far reported, of a hydrogen-bonded supramolecular magnetic material whose properties can be systematically controlled by light.

In this communication, we report a detailed EPR study of the two radicals, *trans*-**1** and *cis*-**1**. We will show that EPR spectroscopy not only provides detailed and definitive information about the electronic struc-

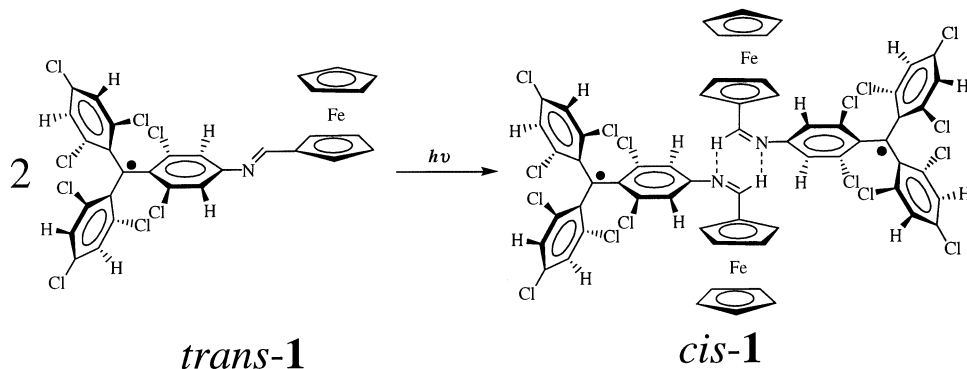
ture of the two isomeric forms but also allows a structural characterization of the supramolecular diradical species.

2. Results and discussion

X-band EPR spectra of a toluene/CH₂Cl₂ (1:1) solution of radical *trans*-**1** were obtained in the temperature range of 220–300 K. EPR spectra measured at 300 K do not provide any specific information about the fine structure of the radical. It is at low temperatures that the spectra show lines corresponding to the coupling of the unpaired electron with the different nuclei with non-zero magnetic moments; i.e. with ¹H, ¹⁴N and naturally abundant ¹³C isotope at the α and aromatic positions. The experimental and simulated spectra of radical *trans*-**1** at 220 K are compared in Fig. 1. Computed simulation gave the isotropic *g*-values (*g*_{iso}) and the isotropic hyperfine coupling constants (*a*_{*i*}) of the unpaired electrons with the different nuclei with non-zero magnetic moments. The *g*_{iso} value for the *trans*-**1** isomer is 2.0030 and the values for the coupling constant are: *a*(¹⁴N) = 1.2 G; *a*₁(¹H) = 1.1 G(6H_{meta}); *a*₂(¹H) = 0.3 G(¹H_{imino}), *a*₁(¹³C) = 28.5 G(1C _{α}); *a*₂(¹³C) =

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Scheme 1.

12.5 G($6H_{\text{orto}}$); $a_3(^{13}\text{C}) = 10.3$ G($3C_{\text{bridge}}$). These values are similar to those previously described for a related ferrocene-based polychlorotriphenylmethyl radical [2].

In contrast, the temperature dependence of a toluene/ CH_2Cl_2 (1:1) solution of radical *cis-1* shows a very specific behavior that differs from that expected for an isolated radical (see Fig. 2). Indeed, EPR spectra measured in the fast-tumbling regime do not provide any specific information about the fine structure of the radical showing a single broad line whose intensity diminishes remarkably on decreasing the temperature.¹ Such behavior differs from that expected for a classical free radical in solution, which implies an increase of the intensities of its EPR lines upon cooling, following the Curie law. Moreover, together with the decrease of the intensity of the central line, the spectra at low temperatures did not show the lines corresponding to the coupling of the unpaired electron with the different nuclei with non-zero magnetic moments. On the contrary, the spectra show the characteristic fine structure of a triplet species.

Why do EPR spectra of radicals *trans-1* and *cis-1* look so different? The most probable reason is that whereas radical *trans-1* remains in solution as an isolated species, the isomer *cis-1* originates a supramolecular dimeric species directed by intermolecular C–H \cdots N hydrogen bonds between $-\text{CH}=\text{N}-$ groups of two different molecules. Indeed, ZINDO/1 semiempirical calculations revealed that the H-bonded dimeric species of *cis-1* correspond to an energy minimum while for the *trans-1* isomer, similar H-bonded dimeric or polymeric species do not correspond to energy minima, probably because of the steric hindrance developed in such spe-

cies [1]. The ZINDO/1 minimized structure of the H-bonded dimeric species of radical *cis-1* is shown in Fig. 3.

The study of the zero-field splitting parameters $|D'|$ and $|E'|$ may provide information on the structure and electronic distribution of the hydrogen-bonded dimeric species. The $|D'|$ parameter reflects primarily the mean distance between the interacting electrons and the $|E'|$ parameter depends mostly on the symmetry of the spin

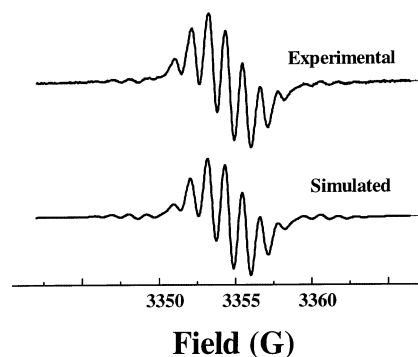


Fig. 1. Experimental and simulated X-band EPR spectra of a toluene/ CH_2Cl_2 (1:1) solution of radical *trans-1* at 220 K.

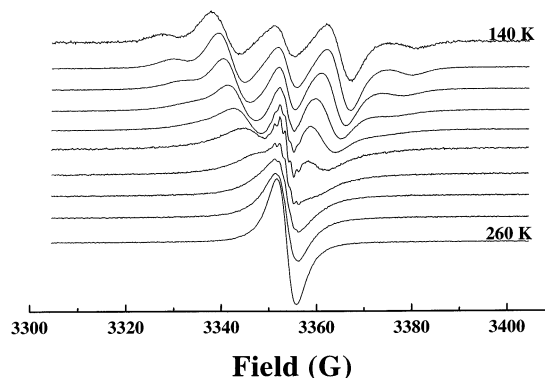


Fig. 2. Temperature dependencies of the X-band EPR of a toluene/ CH_2Cl_2 (1:1) solution of radical *cis-1*.

¹ The decrease of the intensity of the central line due to a crystallization of the radicals, chemical transformation to diamagnetic compounds, or other phenomena were ruled out since the overall signal intensity of the EPR spectra was maintained constant in all the temperature range studied and because of the reversibility of the phenomenon.

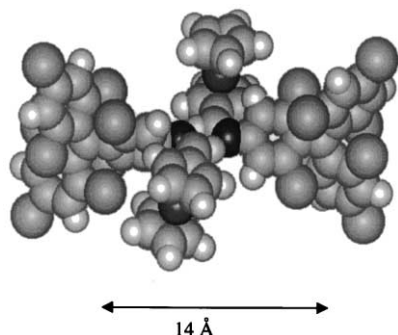


Fig. 3. ZINDO/1 semiempirical optimized structure of the supramolecular hydrogen-bonded dimeric species of *cis*-1.

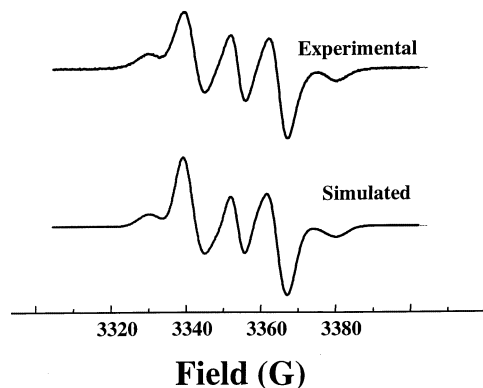


Fig. 4. Experimental and simulated X-band EPR spectra of a toluene/ CH_2Cl_2 (1:1) solution of radical *cis*-1 at 160 K.

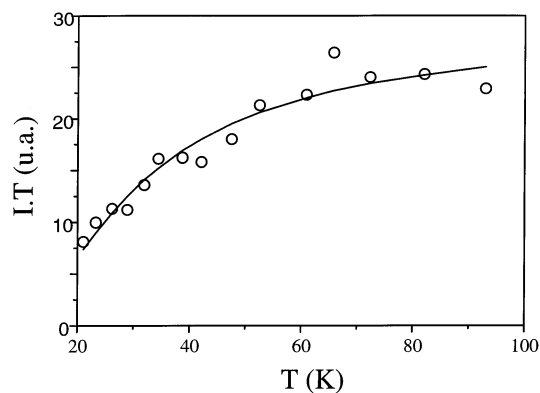


Fig. 5. Temperature dependence of IT of the hydrogen-bonded dimeric species. The closed circles represent the experimental data and the continuous line the fit of the experimental data to the Bleaney–Bowers equation.

density distribution. The absolute values of $|D'| = 25.2 \text{ G}$ and $|E'| = 0 \text{ G}$ were obtained by simulation of the spectra of radical *cis*-1 at 160 K (Fig. 4).²

² The simulation was carried out by superimposition of two types of spectrum: the spectra characteristic of a symmetric triplet species, from where the absolute values of the zero-field splitting parameters were obtained, and a central broad line characteristic of a monoradical species, which is associated with the fraction of the radical (4%) that remains free in solution.

The experimental value of $|E'| = 0 \text{ G}$ suggests that the dimeric species has a low (if any) anisotropy. Moreover, from the absolute value of the zero-field splitting parameter $|D/hc|$, given in cm^{-1} , and using Eq. (1) [3], an average interspin separation of 10.3 \AA was found.

$$r = \left[\frac{3g^2\beta^2}{2hc} \frac{1}{|D/hc|} \right]^{1/3} \quad (1)$$

Such averaged interspin separation is smaller than the nominal separation between the two alpha carbon atoms (*vide supra*) where most of the spin density of polychlorotriphenylmethyl radicals is localized. The through-space distance between the two alpha carbon atoms in the ZINDO/1 minimized structure is 14.0 \AA . This result is in agreement with the existence of a certain degree of electronic delocalization over the imino bridge that reduces the effective separation of the two spins in the diradical species. The electronic delocalization also occurs in the *trans*-1 radical, as stated by the observation of hyperfine coupling constants of the unpaired electron with the ^{14}N atoms of the imino bridge. In fact, such delocalization is not unusual and it has already been observed for a related polychlorotriphenylmethyl diradical covalently linked by a divinylbenzene bridge [4].

Finally, the forbidden $\Delta m_s = \pm 2$ transition characteristic of a triplet species was also observed at the half-field region of the spectrum; the intensity of the corresponding signal (I), obtained by double integration, was measured in the range of 4–100 K. The reproducibility of the results was confirmed by two independent experiments. Since the quantity IT is proportional to the population in the triplet state, the fact that IT (Fig. 5) decreases with decreasing temperature indicates that the ground state of the diradical species is the singlet state and the triplet state should be regarded as a thermally accessible excited state. A separation of $54 \pm 2 \text{ K}$ between both states was obtained from the fitting of the data in Fig. 5 to a Bleaney–Bowers equation [5], which describes the magnetic interaction between dimeric species [6].

The head-to-tail arrangement of the involved radicals favors the presence of antiferromagnetic interactions. However, the relatively large energy gap is difficult to be justified assuming that the spin density is mostly localized on the alpha carbon atoms of the polychlorotriphenylmethyl units, which are far away from each other. It is clear that the existence of a certain degree of delocalization over the imino bridge enhances the presence of magnetic exchange interactions between the two radical units. In some nitronyl nitroxide radicals that aggregate in solution originating supramolecular arrays with a similar head-to-tail geometric arrangement, antiferromagnetic interactions between the involved radicals are also observed [7].

3. Conclusions

We have shown by EPR spectroscopy that the radical *trans*-1 remains isolated in solution whereas the radical *cis*-1 aggregates originating the thermodynamically stabilized hydrogen-bonded diradical species. The experimental averaged interspin separation in the resulting diradical, calculated from the absolute values of the zero-field splitting parameters, is smaller than the nominal separation between the two alpha carbon atoms found in the ZINDO/1 minimized structure. This result is in agreement with the existence of a certain degree of electronic delocalization over the imino bridge that reduces the effective separation of the two spins in the diradical species. Such delocalization plays a crucial role in enhancing the exchange interactions between the two radical units, which are antiferromagnetic in nature. This approach can be extended to the synthesis of novel complexes bearing other organic and inorganic magnetic units providing a valuable access to this interesting class of supramolecular magnetic materials.

4. Experimental

Compounds *trans*-1 and *cis*-1 were prepared as previously described [1]. EPR spectra were recorded on a Bruker ESP-300E spectrometer operating in the X-band (9.3 GHz). Signal-to-noise ratio was increased by accumulation of scans using the F/F lock accessory to guarantee a high-field reproducibility. Precautions to avoid undesirable spectral line broadening such as that arising from microwave power saturations and magnetic field over-modulation were taken. To avoid dipolar broadening, the solutions were carefully degassed three times using vacuum cycles with pure Ar. The g

values were determined against the DPPH standard ($g = 2.0030$). To obtain accurate temperature measurements, between 4 and 100 K, that ensure the validity of the experimental results, the spectrometer was equipped both with a flowing-helium Oxford EPR-900 cryostat, controlled by an Oxford ITC4 temperature control unit, and with a calibrated custom-made double temperature control system for determining accurately the sample temperature.

Acknowledgements

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Ferrocene as a ferromagnetic coupler. Synthesis and characterization of a ferrocene bridged polychlorotriphenylmethyl diradical

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Abstract

A polychlorotriphenylmethyl diradical connected by a 1,1'-ferrocenyldivinylene bridge has been synthesized and characterized. ESR frozen solution experiments down to helium temperature showed that the organometallic unit acts as a ferromagnetic coupler. This fact was supported by ZINDO/1 semiempirical calculations, which showed that the two singly occupied molecular orbitals (SOMOs) are non disjoint in addition to be almost degenerated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferromagnetism; Organic radical; Ferrocene; ESR

1. Introduction

The synthesis and characterization of high-spin macromolecules with purely organic spin-carrier centers have attracted great interest [1]. One of the basic tools to realize such high-spin macromolecules is the *m*-phenylene bridge since it acts as a ferromagnetic coupler when it connects two open-shell units. Indeed, since the Schlenk hydrocarbon, first prepared in 1915 [2], high-spin alignment in the ground state has been successfully demonstrated for several 1,3-phenylene connected carbenes [3] and radicals based on triarylmethyl [4], nitrogen-centered [5] and aminoxyl units [6]. Efforts to increase the number of the aligned spins using 1,3-phenylene couplers have been disturbed by the presence of spin defects and/or bond distortions, which have been shown to affect the ferromagnetic exchange coupling through *m*-phenylenes [7]. To overcome such problems, other complementary approaches such as the use of π -conjugated linear polymers bearing pendant radical groups [8], π -conjugated polycyclic polymers with alternative coupling pathways [9], or the use of diamagnetic metal ions as ferromagnetic couplers [10],

have been used. Indeed, in the case of π -conjugated linear polymers bearing pendant radical groups, the radical units are π -conjugated with the backbone so ferromagnetic interactions take place. The main advantage of these polyradicals is that in spite of the great number of spins accumulated along the polymeric backbone, the ferromagnetic interaction is not sensitive to the spin defects that are unavoidable for macromolecular polyradicals. The main drawback is the weakness of the ferromagnetic interactions obtained with this approach. π -Conjugated polycyclic polymers have also been shown to minimize the interruption of the exchange coupling. Following this approach, a macrocyclic polyradical with an average $S = 10$ below 5 K has been reported [9]. Alternatively, when diamagnetic metal ions are coordinated by radical ligands, those may be assembled so that ferromagnetic spin alignments are obtained. For instance, superexchange through orthogonal magnetic orbitals has been observed in a gadolinium complex octahedrally coordinated by three semiquinone radicals [10].

In our group, we focussed our attention in the development and study of new coupling units able to promote ferromagnetic interactions between pure organic radicals. Metallocenes were excellent candidates to be prospected as magnetic couplers not only because of their rich chemistry but also because they are electroac-

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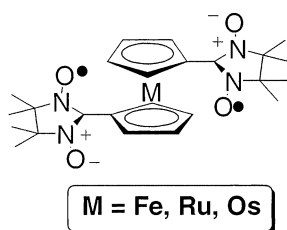


Chart 1.

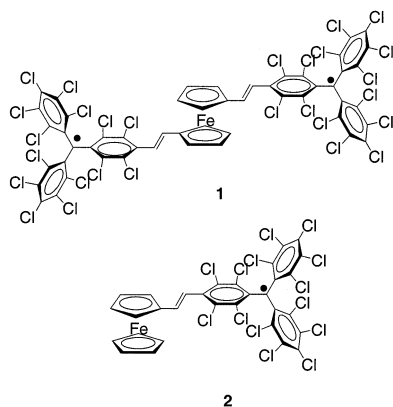
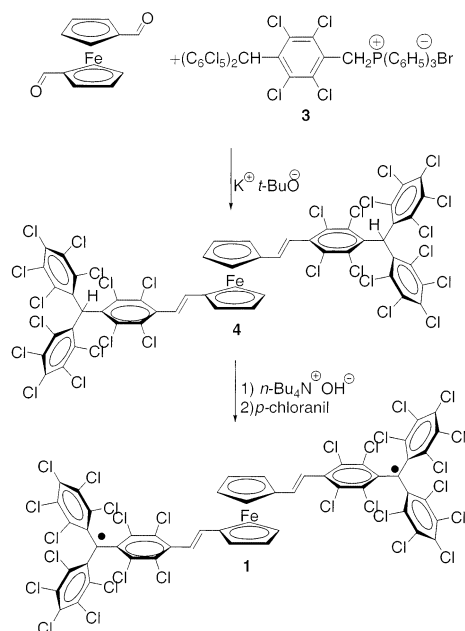


Chart 2.

tive species whose oxidation state can be controlled by means of a chemical or electrochemical stimulus having moreover their oxidized states an open-shell character. However, although metallocenes have been successfully used as building blocks of molecular solids promoting intermolecular magnetic exchange interactions [11], their use as intramolecular magnetic couplers was not studied. Recently, we reported a novel family of compounds consisting of two purely organic α -nitronyl aminoxyl radicals connected by different 1,1'-metallocenylene bridges (see Chart 1). In these compounds, the metallocene units were shown to act as effective magnetic couplers that transmit the magnetic interactions through their skeletons [12]. Nevertheless, the small spin density located on the metallocene units of these systems and the presence of intramolecular hydrogen bonds, which determines the existence of a direct intramolecular through-space magnetic interaction, lead to the appearance of an effective antiferromagnetic interaction between the two α -nitronyl aminoxyl radical units that is very sensitive to the molecular conformation [13]. For this reason, such complexes were not suitable candidates to study and rationalize the behavior of 1,1'-metallocenylene bridges as magnetic couplers.

In order to overcome both inconvenients, diradical **1** consisting of two polychlorinated triphenylmethyl radicals connected by a 1,1'-ferrocenyldivinylene bridge, was designed [14]. The particular structure and topology of such a diradical allow us to expect a non-negligi-



Scheme 1.

ble spin density on the ferrocene moiety making feasible the magnetic coupling between the two organic radical units. In addition, the location of both radical units far away from each other avoids any possibility of having intramolecular hydrogen bond interactions, and consequently, a significant direct through-space magnetic interaction (Chart 2).

2. Results and discussion

2.1. Synthesis of ferrocenyl diradical **1**

As outlined in Scheme 1, the synthetic route for preparing diradical **1** is based on two main steps. First, a Wittig reaction between the corresponding ferrocene dicarboxaldehyde derivative and the phosphonium bromide precursor **3** that yields the π -conjugated hydrocarbon **4**. Second, the deprotonation of hydrocarbon **4** and the subsequent oxidation of the resulting dicarbanion to yield the desired diradical **1**.

In the first step of the synthesis of **1**, the {4-[bis(2,3,4,5,6-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzyl}(triphenyl)-phosphonium bromide (**3**) [19] was reacted with ferrocene 1,1'-biscarboxaldehyde to give (*E,E*)-1,1'-divinylferrocene- β,β' -ylene-bis-(4-tetrachlorotriphenylmethane) (**4**). This reaction is strongly stereoselective since it yields exclusively the *E,E* isomer as ascertained by IR and $^1\text{H-NMR}$ data [15]. Such stereoselectivity is justified if we consider that the ylide derived from the phosphonium bromide is stabilized by the presence of a polychlorinated aromatic ring. In addition, the *Z/E* isomer distribution of the Wittig products is also strongly influenced by the nature of the

base used in the preparation of the ylide [16]; being the potassium *tert*-butoxide, used in this work, the base of choice for maximizing the yields of *E*-olefins [17]. Finally, a THF solution of **4** was treated with an excess of $n\text{-Bu}_4\text{N}^+\text{OH}^-$, and the resulting dianion was oxidized with *p*-chloranil to yield the (*E,E*)-1,1'-divinylferrocene- β,β' -ylene-bis-(4-tetradecachlorotriphenylmethyl) diradical (**1**), which was isolated as a clathrate ($1 \cdot 2\text{C}_6\text{H}_6$) after chromatographic purification and recrystallization from C_6H_6 . The resulting diradical, which is completely stable in air both in the solid state and in diluted solutions, was obtained as dark green microcrystals that were characterized by elemental analysis, cyclic voltammetry, IR, UV–vis and ESR spectroscopies.

Interestingly, diradical **1** retained the *E,E* configuration of its precursor, as ascertained by spectroscopic data, in spite of the use of a strong base and an oxidizing agent [19].

2.2. Electrochemical studies

Electrochemical studies of **1** in CH_2Cl_2 , with $n\text{-Bu}_4\text{NPF}_6$ (0.1 M) as supporting electrolyte and using a Pt wire as a working electrode, were done at room

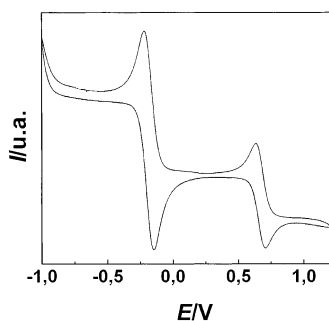


Fig. 1. Cyclic voltammogram, recorded in a CH_2Cl_2 solution containing Bu_4NPF_6 (0.1 M), of diradical **1**.

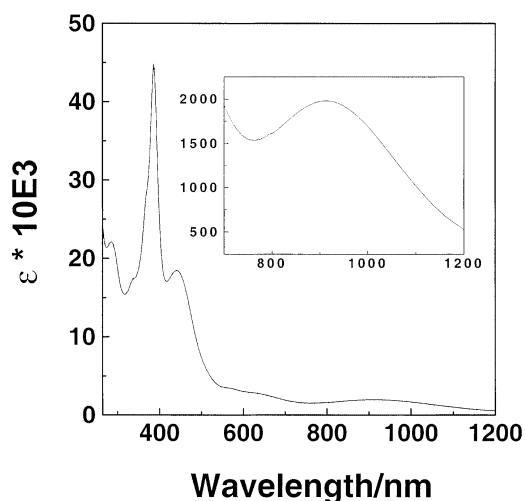


Fig. 2. UV–vis–near IR spectra of diradical **1** in THF.

temperature. The cyclic voltammetry of diradical **1** (Fig. 1) shows one reversible oxidation process at +666 mV and one reversible reduction process at –181 mV (vs. Ag/AgCl), that involves the simultaneous transfer of two electrons.

The oxidation process was assigned to the oxidation of the ferrocene unit, while the reduction process was assigned to the simultaneous reduction of both triphenylmethyl radical units. This result suggests the presence of a very weak or negligible electronic interaction between the triphenylmethyl units since in the case of a strong or moderate electronic interaction between the two units, two electrochemical waves are anticipated. Only if both units exhibit very weak or negligible electronic interactions, the two standard redox potentials must be very close and a single two-electron wave will be observed, with minor differences in shape with respect to a true bielectronic process. The cyclic voltammetric peak separation of the reversible reduction waves (90 mV), which is close to the expected theoretical separation of 59 mV, serves as a criterion to unequivocally assign the electrochemical reversibility of the process. The slightly higher peak separation may arise from the high resistance of the solutions used for the measurements. It is also important to emphasize that the oxidation process of the ferrocene unit of diradical **1** appears at a higher potential value than those observed for the related monoradical species **2** and the unsubstituted ferrocene [14]. This fact is the first direct evidence for the presence of an electronic interaction between the radical and the ferrocene units.

2.3. UV–vis–near IR spectroscopy

Electronic absorption spectra of polychlorotriphenylmethyl radicals usually show an intense absorption band at 386 nm and two weaker bands centered between 565 and 605 nm, all of which are assigned to the radical character of the triphenylmethyl units [18]. The absorption spectra of diradical **1** (Fig. 2) shows an intense absorption at 387 nm ($\epsilon = 44\,900$) and a weaker band at 442 nm ($\epsilon = 18\,500$). The band at 442 nm is unprecedented in unsubstituted chlorinated triaryl-methyl radicals and can be therefore ascribed to a large electronic delocalization of the unpaired electron into the π -conjugated system. A similar absorption has been recently observed in a *p*-divinylbenzene diradical [19], which also exhibits a large electronic delocalization.

More interesting is the observation for diradical **1** of a weak absorption at 900 nm ($\epsilon = 2000$), which is not observed for simple polychlorotriphenylmethyl radicals nor for simple ferrocene units. Two weak bands at 325 and 440 nm dominate the spectrum of ferrocene [20]. The shorter wavelength band ($\lambda = 325$ nm) is assigned to $\text{Fe}(d\pi) \rightarrow \text{Cp}(\pi^*)$ charge transfer, $\pi \rightarrow \pi^*$ transitions, or a combination of these, whereas the longer wave-

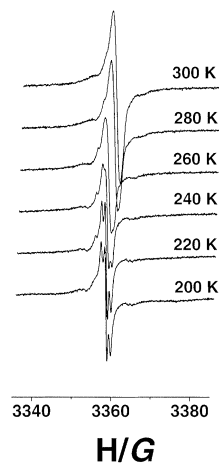


Fig. 3. Temperature-variable ESR isotropic spectra of a toluene/chloroform (1:1) solution of diradical **1**.

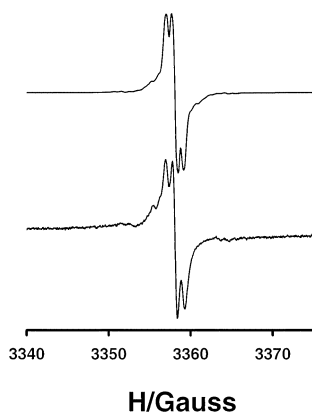


Fig. 4. Experimental (top) and simulated (bottom) isotropic solution EPR spectra of diradical **1** (right) in a toluene/chloroform (1:1) solution at 200 K.

length ($\lambda = 440$ nm) is assigned to a d-d transition within the ligand field formalism. It is true that upon substitution of one of the Cp rings of ferrocene with conjugated acceptors, one would expect changes of the visible spectra. Although the position and intensity of the ferrocene bands depends upon the nature of the chromophore acceptor group, shifts up to 520 nm and intensities of $\epsilon = 10\,000$ have been reported. However, neither the position nor the intensity of the band appearing at 900 nm may be assigned to intrinsic ferrocene transitions. Most likely, such band may be assigned as an intervalence band transition associated with an intramolecular electron transfer from the ferrocene unit (donor) to the radical unit (acceptor). Similar intervalence band transitions have already been observed in mixed-valence complexes containing ferrocenylpyridine and rutheniumammines [21]. Moreover, the concentration-dependence of the intervalence band follows the Beer–Lambert law, confirming that the electron transfer should have an intramolecular rather than an intermolecular character.

2.4. ESR spectroscopy

X-band ESR isotropic spectra of a toluene/chloroform (1:1) solution of diradical **1** were obtained in the temperature range of 180–300 K (see Fig. 3). The poor resolution achieved at high temperatures (300–240 K) does not permit to extract any specific information about the electronic distribution of the diradical. By contrast, the resolution increases considerably at low temperatures (240–190 K) showing the lines corresponding to the coupling of the unpaired electron with the different nuclei with non-zero magnetic moments; i.e. with ^1H and naturally abundant ^{13}C isotope at the α and aromatic positions.

The experimental and simulated spectra of diradical **1** at 220 K are compared in Fig. 4. Computer simulation gave the isotropic g -values (g_{iso}) and the isotropic hyperfine coupling constants (a_i) of the unpaired electrons with the different nuclei with nonzero magnetic moments. The g_{iso} value for diradical **1** is 2.0028, which is very close to that observed for other polychlorotriphenylmethyl radicals [18]. More interesting is the comparison of the isotropic hyperfine coupling constant values with the hydrogen atoms of the ethylene moieties and some of the carbon nuclei of the triphenylmethyl unit. The values of the coupling constants of diradical **1**, $a(^1\text{H}) \approx 0.80$ G (2H), $a(^1\text{H}) \leq 0.30$ G (2H), $a(^{13}\text{C}) \approx 13.0$ G (1 C_α) and $a(^{13}\text{C}) \approx 6.0$ G (1 C_{bridge}) are approximately half than those found for the related ferrocenyl monoradical **2**, $a(^1\text{H}) \approx 1.77$ G (1H), $a(^1\text{H}) \approx 0.57$ G (1H), $a(^{13}\text{C}) \approx 29.0$ G (1 C_α), and $a(^{13}\text{C}) \approx 11.0$ G (1 C_{bridge}). It is then possible to conclude that the two electrons in diradical **1** are magnetically interacting with an exchange coupling constant, J , that fulfills the following condition $|J| \gg |a_i|$.

In agreement with this result, the spectrum of diradical **1** in a frozen toluene/ CH_2Cl_2 (1:1) mixture shows the characteristic fine structure of a triplet species. The zero-field splitting parameters obtained by computer simulation of the spectra obtained at 160 K are $|D'| = 48$ G and $|E'| = 0$, indicating that this complex has a low (if any) anisotropy. The forbidden $\Delta m_s = \pm 2$ transition characteristic of triplet species, is also observed at the half-field region of the spectrum and the intensity of the corresponding signal (I_{pp}), obtained by double integration, was measured in the 4–100 K temperature region. Since the quantity $I_{\text{pp}}T$ is proportional to the population in the triplet state, the fact that $I_{\text{pp}}T$ (Fig. 5) increases with decreasing temperature indicates that the ground state of **1** is the triplet state and the singlet state should be associated with a thermally accessible excited state. A separation of $+10$ K (7 cm^{-1}) between both states was obtained from the fitting of the $I_{\text{pp}}T$ versus T plot to the Bleaney–Bowers equation [22].

2.5. Semiempirical calculations

In order to understand why the ferrocene unit acts as a ferromagnetic coupler in diradical **1**, we have performed ZINDO/1 semiempirical calculations. It should be noted that full geometry optimization with configuration interaction (CI) is an extremely time demanding process, especially when a large number of heavy atoms are involved (as is the case for diradical **1**). A reasonable alternative consisted in carrying out the geometry optimization with an UHF wave-function. The optimized structure is then used as input geometries for a single-point CI calculation, which allowed a more accurate estimation both of the electronic properties, molecular orbitals and energy minima. The optimized structure of diradical **1** obtained in such a way (Fig. 6) has an extended S-shaped profile that is very close to that of an ideal centrosymmetrical molecule with an inversion center on the metal nucleus. Such profile results in a significantly large through-space distance

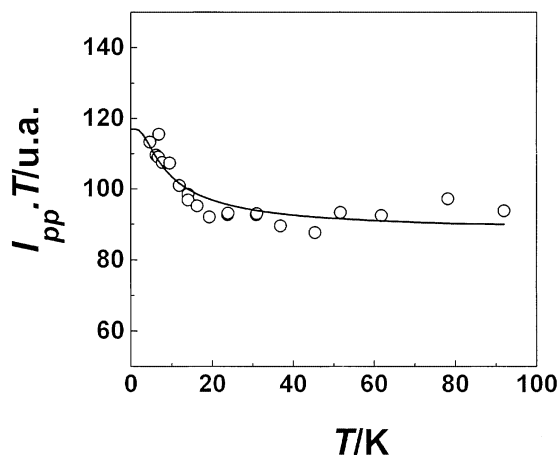


Fig. 5. Temperature dependence of the $I_{pp} \cdot T$ of diradical **1**. The closed circles represent the experimental data and the continuous lines the fit of experimental data to the Bleaney–Bowers equation.

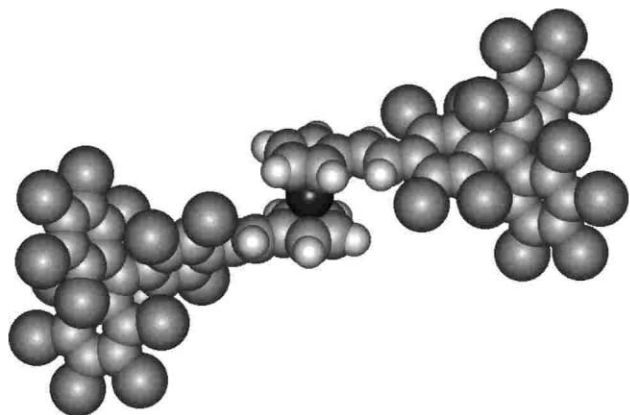


Fig. 6. ZINDO/1 semiempirical optimized structure of diradical **1**.

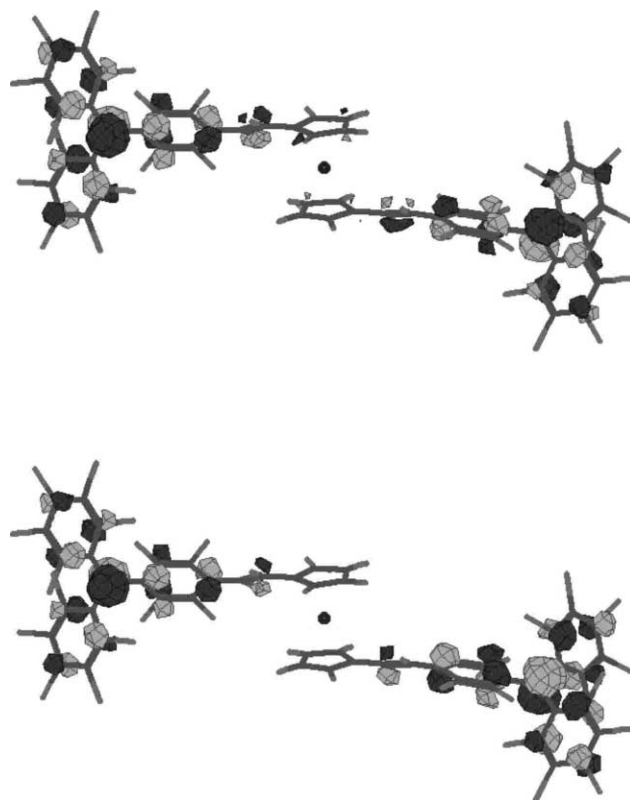


Fig. 7. Representations of the two SOMO orbitals of diradical **1** according to ZINDO/1 calculations.

between the two radical centers (19 Å). The dihedral angles of the inner aromatic group of the triphenylmethyl units, with respect to their adjacent vinylene moieties, are 28.2 and 29.1°, which deviates from coplanarity. In addition, the two vinylene moieties are bent and twisted out of the plane defined by the Cp rings with small dihedral angles of 4.9 and 8.3°.

The ferromagnetic coupling of the unpaired electrons of diradical **1** to give a triplet ground state can be justified in terms of elementary molecular orbital considerations. Indeed, the key to predict the spin multiplicity of an organic biradical from a molecular orbital viewpoint is to determine whether the singly occupied molecular orbitals (SOMOs) have (non-disjoint) or do not have (disjoint) coefficients on a common set of atoms, since this is a prerequisite for Coulombic repulsion between the two electrons to become operative. If the SOMOs orbitals are non-disjoint and degenerate, then the Pauli exclusion principle favors the parallel spin alignment stabilizing the high-spin state. In the case of diradical **1**, the SOMO orbitals not only are almost degenerated with an electronic energy difference less than 0.05 eV, but they are also coextensive in most part of the molecule justifying the high-spin ground state experimentally observed (Fig. 7).

3. Conclusions

Diradical **1** consisting of two polychlorinated triphenylmethyl radicals connected by a 1,1'-ferrocenyldivinylene bridge, has been synthesized and characterized. Interestingly, ESR experiments showed that the 1,1'-ferrocenylene bridge acts as a ferromagnetic coupler of two radical units connected to it. This result was justified theoretically by ZINDO/1 semiempirical calculations. The use of ferrocene as a ferromagnetic coupler can be extended to the synthesis of novel high-spin metallocene complexes bearing other open-shell organic and inorganic units providing a valuable access to this interesting class of materials.

4. Experimental

4.1. General procedures

All solvents were reagent grade from SDS and were used as received and distilled otherwise indicated. All reagents, organic and inorganic, were of high purity grade and obtained from E. Merck, Fluka Chemie and Aldrich Chemical Co. Elemental analyses were obtained in the Servei de Microanàlisi del CID (CSIC), Barcelona.

EPR spectra were recorded on a Bruker ESP-300E spectrometer operating in the X-band (9.3 GHz). Signal-to-noise ratio was increased by accumulation of scans using the F/F lock accessory to guarantee a high-field reproducibility. Precautions to avoid undesirable spectral line broadening such as that arising from microwave power saturation and magnetic field overmodulation were taken. To avoid dipolar broadening, the solutions were carefully degassed three times using vacuum cycles with pure argon. The *g* values were determined against the DPPH standard (*g* = 2.0030). Electrochemical experiments were performed with an Electromat 2000 system (ISMP Technologies), using a platinum wire as working electrode and a saturated calomel electrode (Ag/AgCl) as reference electrode. Anhydrous CH₂Cl₂ was freshly distilled over P₂O₅ under nitrogen. Commercial tetrabutylammonium hexafluorophosphate (Fluka, electrochemical grade) was used as the supporting electrolyte. UV-vis and near-IR were recorded using a Varian Cary 05E spectrophotometer. The ¹H-NMR spectra were recorded with Bruker FT80 spectrophotometer (¹H-NMR 80 MHz).

The geometry of diradical **1** was minimized using ZINDO/1 semiempirical calculations. These calculations were performed using the HyperChem 5 molecular modelling package. The initial input geometries (excluding the propeller-like arrangement of each triaryl moiety) were kept planar, i.e. the dihedral angles defined by the vinylene moieties and the phenylene

rings were set to 0°. Moreover, for each diradical, two different initial input conformations differing by a 180° rotation around one of the single bonds that connects the central phenylene unit and one of the vinylene moieties, were used. It is important to notice that independently of the input model used, the minimized geometries converged in similar close-lying minima with almost identical structures.

4.2. (*E,E*)-1,1'-Divinylferrocene-β,β'-ylene-bis-(4-tetradecachlorotriphenylmethane) (**4**)

Potassium-*tert*-butoxide (46 mg, 376.4 μmol) and {4-[bis(2,3,4,5-pentachlorophenyl)methyl]-2,3,5,6-tetrachlorobenzyl}(triphenyl)-phosphonium bromide monoadduct (**3**) (395 mg, 340.44 μmol) were suspended in ca. 10 ml of dry THF. The yellow ylide suspension that formed immediately was stirred for 70 min. Then the ferrocene 1,1'-biscarbaldehyde (39 mg, 160 μmol) was added and the system was stirred for a further 72 h. The reaction mixture was quenched with 5 ml of 2 N HCl and extracted with four portions of 25 ml of chloroform. The organic layer was washed with 20 ml of water, dried with NaSO₄ and evaporated under reduced pressure. Finally, chromatographic purification with silica and *n*-hexane/CHCl₃ (1:1) yield 145 mg (53.3%) of pure **4**.

Anal. Calc. for C₅₂H₁₄Cl₂₈Fe: C, 37.02; H, 0.84. Found: C, 37.06; H, 0.72%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$: 2925, 1634, 1533, 1369, 1338, 1299, 1241, 1138, 1045, 960, 810, 715, 685, 649, 531, 479. ¹H-NMR (CDCl₃, Me₄Si): 4.44 (s, 4H, cyclopentadienyle subst.), 4.51 (s, 4H, cyclopentadienyle subst.), 6.69 (d, 2H, *J*_{trans} = 10.8 Hz, vinylene), 6.94 (d, 2H, *J*_{trans} = 10.8 Hz, vinylene), 7.03 (s, 1H, methane).

4.3. (*E,E*)-1,1'-Divinylferrocene-β,β'-ylene-bis-(4-tetradecachlorotriphenylmethyl) diradical (**1**)

Tetrabutylammonium hydroxide (40% in water, 1.5 M, 131 μl, 197 μmol) was added to a solution of **4** (133 mg, 78.8 μmol) in 15 ml of THF. The solution, which immediately turned purple was stirred at room temperature (r.t.) for 4 h. Subsequent oxidation of the resulting dianion with *p*-chloranil (53.6 mg, 220 μmol) was performed and the resulting solution was left at r.t. for 35 min. Finally the solvent was eliminated under reduced pressure and the product was purified by column chromatography using hexane in silicagel tetrachloro-carbon (1:1) to yield 60 mg (45.2%) of pure **1**.

Anal. Calc. for C₅₂H₁₂Cl₂₈Fe·2C₆H₆: C, 41.80; H, 1.40. Found: C, 42.20; H, 1.65%. $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$: 2923, 2853, 1716, 1623, 1507, 1645, 1337, 1319, 1261, 1156, 1119, 1046, 959, 945, 869, 817, 735, 712, 699, 652, 561, 530, 475, 417.

Acknowledgements

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- [13] The spin density on the metallocene units linked to the α -carbon atom of α -nitronyl aminoxy radicals is very small because the SOMO orbital has a node on this carbon atom and therefore the spin density is transmitted only by a spin polarization mechanism. On the contrary, in the case of diradical **1** both unpaired electrons can be delocalized by conjugation onto the ferrocene unit according with the particular topology of the diradical promoting a larger magnetic coupling.
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Nonlinear optical properties of a new stable ferrocenyl Schiff-base polychlorotriphenylmethyl radical

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Abstract

Here we report the NLO properties of the isomeric *trans* and *cis* forms of radical **1**. This fact allowed us to prove the feasibility of polychlorotriphenylmethyl radicals as building blocks with electron acceptor ability for NLO materials. Moreover, by comparing the β_{vec} values obtained for isomers *trans*-**1** and *cis*-**1** with those of related ferrocenyl-based chromophores, we propose that molecular torsions strongly decrease the second-order NLO response.

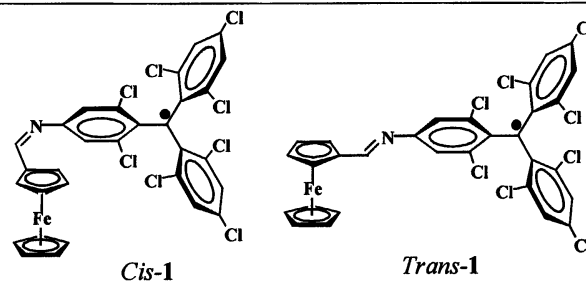
Keywords: Triphenylmethyl radical, *cis-trans*, nonlinear optics

1. Introduction

In the last few years, a large interest has been devoted to the investigation and development of NLO materials having *open-shell* electronic structures. As it has been recently pointed out,¹ species having *open-shell* electronic states, such as organic radicals, can exhibit very large first-order hyperpolarizability (β) in comparison with analogous *closed-shell* systems, thanks to the presence of accessible low-lying charge transfer electronic states. Despite this fact, scant examples of organic *open-shell* species showing NLO responses have been reported, mostly due to the inherent low persistency and large photo-optical instability of these species.²

For this reason, we focussed our attention in the synthesis and characterization of new NLO materials using polychlorinated triphenylmethyl (PTM) radical units as building blocks. The interest for these radicals is twofold. First, their low reduction potentials indicate that they may act as effective electron acceptor units. Second, these radicals have their *open-shell* centers sterically shielded by six bulky chlorine atoms in order to increase their life expectancies and thermal and chemical stabilities.³

In a previous communication we reported the possibility to synthesize, isolate and characterize the *trans* and *cis* isomers of the ferrocenyl schiff-base polychlorotriphenylmethyl radical (**1**).⁴ In this communication, we report for the first time the NLO properties of both isomeric forms, *trans*-**1** and *cis*-**1**.



2. Experimental

Compounds *trans*-**1** and *cis*-**1** were obtained as previously described. $\mu\beta$ values were measured with a nonlinear optics spectrometer from SOPRA S.A. The fundamental source at 1907 nm came from the first Stokes peak of a hydrogen Raman cell pumped by the 1064 nm light of a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns pulse). The resulting beam light was passed through a linear polarizer and focused on the EFISH cell. The applied DC electric field (parallel to the light polarization) was 7 kV. The output light of the cell was passed through an interference filter to select the second harmonic light, which was detected with a R642 photomultiplier from Hamamatsu. All the experiments were carried out in CH_2Cl_2 irradiating at $\lambda = 1907$ nm. μ values were calculated from the minimized ZINDO/1 structures.

3. Nonlinear optical properties

Donor-Acceptor systems are one of the most developed structures in the search for new compounds with efficient

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NLO responses.⁵ *Trans*-1 and *cis*-1 fulfill such a donor-acceptor structure, where the ferrocene is acting as a donor unit, the triphenylmethyl radical is acting as an acceptor unit, and both are connected through a conjugated $-\text{CH}=\text{N}$ -bridge. This is the first example of a NLO material that combines an *open-shell* organic radical as the acceptor unit and a ferrocene moiety as the donor group. The synergism of both units was expected to drastically increase the NLO of such a material.

In agreement with our expectancies, attachment of an organic radical acceptor to the ferrocene unit results in the observation of a second-order NLO response. The β_{vec} values found for *trans*-1 and *cis*-1 isomers are shown in Table 1.

Table 1.
NLO properties of *trans*-1 and *cis*-1

| | λ_{max} (nm) ^a | $\mu\beta \cdot 10^{-48}$ esu | $\mu \cdot 10^{-18}$ esu | $\beta \cdot 10^{-30}$ esu |
|--------------|---|----------------------------------|-----------------------------|-------------------------------|
| <i>Cis</i> | 566 | 100 | 7,92 | 12,6 |
| <i>Trans</i> | 563 | 106 | 8,38 | 12,6 |

As far as we know, compound 1 is the second radical-based chromophore whose second-order NLO properties have been measured using the EFISH technique. The first one was the pure organic *p*-nitrophenyl α -nitronyl nitroxide radical, described by Zyss *et al.*,⁶ which gave a β_{vec} value of 6.24×10^{-30} esu. On the other hand, the β_{vec} values found for *trans*-1 and *cis*-1 isomers closely resemble those previously reported for similar ferrocene-based chromophores of the form $(\text{C}_5\text{H}_5)\text{Fe}(\text{C}_5\text{H}_4)-(\text{CH}=\text{CH})-p\text{-C}_6\text{H}_4\text{-Y}$, where Y stands for groups of different acceptor strength capacities.⁷ Thus, the expected synergic behavior in the combination of ferrocene donor and PTM acceptor does not appear in compound 1. This fact may arise from the presence of unexpected molecular torsions, which disturb the coplanarity of the molecular systems. In order to assess such possibility, ZINDO/1 semiempirical calculations were used. The ZINDO/1 minimized geometry of both isomers show a strong torsion between the phenyl unit and the C=C=N-C plane making a dihedral angle of 55°. To better illustrate this fact the ZINDO minimized structure of isomers *trans*-1 and *cis*-1 are shown in Fig. 1.

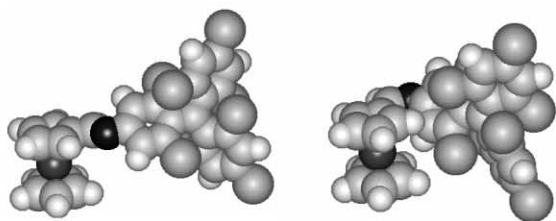


Fig. 1. *Trans*-1 and *cis*-1 minimized structures using a semiempirical ZINDO/1 method.

Such torsion probably arises from the overlap between the lone pair electrons on the nitrogen and the π system of the

phenyl ring. The lack of coplanarity leads to a poor π conjugation in the system and, therefore, to the obtaining of lower β_{vec} values than those initially expected. The same arguments can be used to explain the similar β_{vec} values found for the isomeric forms, *trans*-1 and *cis*-1, while considerable differences between the second-order NLO responses of two isomers were expected.⁷

4. Conclusions

In summary, we have reported the second-order NLO properties of compounds *trans*-1 and *cis*-1. This fact allowed us to prove the feasibility of polychlorotriphenylmethyl radicals as building blocks with electron acceptor ability for NLO materials. Moreover, by comparing the β_{vec} values obtained for isomers *trans*-1 and *cis*-1 with those of related ferrocenyl-based chromophores, we propose that molecular torsions strongly decrease the second-order NLO response. Further studies directed towards the synthesis and characterization of new ferrocene-based organic radical chromophore are being pursued nowadays in our laboratory. Such ferrocene-based organic radical chromophore use an ethylene bridge, which is expected to give rise to a more coplanar structure and therefore to an enhancement of the NLO properties of this kind of materials. The use of a nonamethylated ferrocene unit is also expected to enhance the NLO properties of the system thanks to its higher donor ability.

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Nonlinear optical properties of polychlorotriphenylmethyl radicals: towards the design of ‘super-octupolar’ molecules

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Abstract

Molecular quadratic hyperpolarizability (β_c) of substituted polychlorinated triphenylmethyl radicals, **1–8**, has been determined by using the harmonic light scattering (HLS) technique. Results showed that this *opens-shell* family known to possess a good chemical stability also exhibited a very large SONLO response. The presence of a permanent dipole moment in the ground state for some of these octupolar compounds makes them attractive candidates for further orientation by the poling technique. Data of compounds **1–8** have been discussed on the basis of a model describing the evolution of the β_c response for D_{3h} and C_{2v} symmetry groups. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In the last decade, the interest in molecular design for the development of novel second-order nonlinear optical (SONLO) materials has considerably increased due to their potential applications in emerging optoelectronic technologies [1]. In this regard, organic compounds have received remarkable attention mainly due to their synthetic diversity. Most of the organic materials that

exhibit large microscopic second-order nonlinearity, β , consist of molecular structures in which strong electron-donating (D) and withdrawing (A) groups are connected through conjugated π -electron moieties. The major drawback of these D–A unidimensional systems is that strong nonlinearity is antagonized by a strong absorption at the visible harmonic wavelength. In the last few years, octupolar molecules belonging to planar T_d , D_{3h} or C_{3v} and nonplanar D_3 or C_3 symmetry groups have been proposed to improve the balance between the transparency and the SONLO signal [2,3]. Among octupolar compounds, organometallic and coordination molecules have attracted the attention of both physicists and chemists since a wide range of

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metals with different oxidation states, as well as a large choice of ligands and geometries, may be obtained [2–7]. Various strategies are currently employed to further increase the molecular SONLO activity, such as the extension of the π -electron system, introduction of stronger D,A-groups [4] or the use of paramagnetic metal centers [5–7]. In this latter case, studies of the metal electronic configuration in planar [5,6] or in octahedral [7] geometry revealed that species having *open-shell* electronic states exhibit larger β values than analogous *closed-shell* systems. These results pointed out the possibility of using purely organic free radicals as molecules with large SONLO activities since their *open-shell* electronic states permit to expect the presence of accessible low-lying charge transfer electronic states enhancing the β values with respect to their *closed-shell* counterparts. In the present Letter, we will report the SONLO properties of substituted polychlorinated triphenylmethyl radicals by using harmonic light scattering (HLS) experiments. This family of radicals has been selected due to a remarkable high thermal, chemical, and photo-optical stability in contrast to the previous examples of organic radicals [6,8–13].

The polychlorinated triphenylmethyl radicals family has also been investigated because it is an opportunity to study the SONLO properties of open-shell octupolar molecules with permanent dipole moment in the ground state. In fact, a current challenge is the macroscopic organization of octupolar compounds in a noncentrosymmetric environment. In traditional D–A unidimensional systems several methods are well known, such as crystal engineering, LB films or electric field-induced orientation, while in octupolar compounds results are very limited. Theoretically, purely octupolar molecules show no ground-state dipole moment and thus are promising candidates for crystalline materials, as the lack of a dipole moment should favor a noncentrosymmetric arrangement [14,15]. But most purely octupolar compounds crystallize in a centrosymmetric arrangement and the absence of a permanent dipole moment prevents from poling by a static electric field. Macroscopic noncentrosymmetry order has been only induced by the recently developed all-

optical poling method [16,17]. Nevertheless, poling by a static electric field remains a method of choice since its particularly simple. Therefore, one may want to find a strategy to improve the SONLO properties of a molecular organization while preserving the existence of a permanent dipole moment at the molecular level. Data obtained on polychlorinated triphenylmethyl radicals will be then discussed and a model will be proposed.

2. Experimental

Reagents were obtained commercially and used as purchased. Synthesis of polychlorinated triphenylmethyl radicals, **1–8**, and X-ray crystal structures were reported previously [18–23]. Absorption and fluorescence were recorded on a Cary 5E spectrophotometer and Edinburgh Instruments spectrometer, respectively. Note that absorption at 532 is small and almost similar for all the investigated compounds. Therefore the resonant enhancement of β_c at the harmonic laser frequency is expected to be similarly weak and cannot account for the general trend we presented in Table 1. Fluorescence spectra were collected with spectroscopic solvents quality. The standard for the fluorescence quantum yield determinations with solvent refractive index correction was quinine bisulfate in 1 N H₂SO₄ ($\phi_f = 0.55$) and the experimental errors are $\pm 10\%$. All compounds have been investigated at 532 nm. Weak emissions have been recorded for **1** ($\phi_f = 0.09$), **2** ($\phi_f = 2 \times 10^{-3}$), **5** ($\phi_f = 0.19$), **6** ($\phi_f = 3 \times 10^{-3}$) and **8** ($\phi_f = 0.04$). Nevertheless, no direct correlation between emission and measured β_c value of Table 1 has been noticed.

Molecular nonlinear coefficient were performed in dichloromethane solution using the HLS experiment [24,25]. In fact, some of the investigated compounds belong to the D₃ symmetry groups and the traditional electric field induced second harmonic generation (EFISH) measurements were ruled out. The quadratic hyperpolarizability (β) was derived from the intensity ($I_{2\omega}$) of the incoherent scattered light at 532 nm according to

$$I_{2\omega}/(I_{\omega}^0)^2 = G(N_s\beta_s^2 + N_c\beta_c^2)e^{-N_c\sigma_{2\omega}l}, \quad (1)$$

Table 1
Numbering of the polychlorinated triphenylmethyl radicals, Ar¹Ar²Ar³C[•], studied

| Radicals | Ar ¹ | Ar ² | Ar ³ | λ_{\max} (log ϵ) ^a | β_c (log ϵ_{532}) |
|----------|--|--------------------------------------|--------------------------------------|---|-----------------------------------|
| 1 | C ₆ Cl ₅ | C ₆ Cl ₅ | C ₆ Cl ₅ | 385 (4.5) 514 (3.0) 566 (3.0) | 362 (2.9) |
| 2 | 4H–C ₆ Cl ₄ | C ₆ Cl ₅ | C ₆ Cl ₅ | 382 (4.5) 510 (3.0) 562 (3.0) | 363 (3.0) |
| 3 | 4CH ₃ –C ₆ Cl ₄ | C ₆ Cl ₅ | C ₆ Cl ₅ | 383 (3.7) 504 (2.3) 560 (2.3) | 118 (2.2) |
| 4 | 3H,5H–C ₆ Cl ₃ | C ₆ Cl ₅ | C ₆ Cl ₅ | 382 (4.6) 507 (3.0) 556 (3.0) | 407 (3.0) |
| 5 | 4H–C ₆ Cl ₄ | 4H–C ₆ Cl ₄ | 4H–C ₆ Cl ₄ | 373 (4.4) 486 (2.8) 574 (2.7) | 237 (2.9) |
| 6 | 3H,5H–C ₆ Cl ₃ | 3H,5H–C ₆ Cl ₃ | 3H,5H–C ₆ Cl ₃ | 373 (4.6) 496 (2.9) 540 (2.9) | 755 (2.9) |
| 7 | C ₆ Cl ₅ | 3H,5H–C ₆ Cl ₃ | 3H,5H–C ₆ Cl ₃ | 378 (4.8) 504 (3.2) 547 (3.2) | 593 (3.2) |
| 8 | 3H,4NH ₂ ,5H–C ₆ Cl ₂ | 3H,5H–C ₆ Cl ₃ | 3H,5H–C ₆ Cl ₃ | 378 (4.4) 421 (3.8) 543 (3.3) 575 (3.5) | 262 (3.3) |

Absorption maxima (λ_{abs} , nm), molar extinction coefficients (ϵ , l mol⁻¹ cm⁻¹), quadratic molecular hyperpolarizability (β_c , 10⁻³⁰ esu) and molar extinction coefficients at 532 nm (ϵ_{532} , l mol⁻¹ cm⁻¹) in dichloromethane at room temperature.

^aNo modifications of either the general shape or the position of the maxima were observed before and after the SONLO experiments.

where I_{ω}^0 is the incident laser intensity and G is a constant relative to the collection and quantum efficiencies. The subscripts s and c denote solvent and molecule, respectively, while N is the number density of each component, $\sigma_{2\omega}$ is the molecular cross-section at the harmonic frequency and l is the effective optical path length.

The Q -switched Nd³⁺:YAG laser operating at 1064 nm yields a pulse of 10 ns duration at 10 Hz repetition rate. The incident pulse intensity is changed by a set composed of a computer controlled rotating half-wave plate followed by a Glan–Taylor polarizer. The fundamental laser beam was focused on the center of the 2 cm path quartz cell with a long focal length plano-convex lens ($f = 150$ mm). The light scattered perpendicular to the incident beam was detected with a photomultiplier tube (PMT). A low-pass filter was used to filter out Rayleigh scattered infrared light. An interference filter (532 nm central wavelength and 3 nm transmission bandwidth) permitted a second harmonic detection. The electrical signal from the PMT is first amplified then digitized by a lab-made box-car. The accuracy of our setup on the determination of β was checked on a p -nitroaniline sample in methanol. The error is estimated to be approximately $\pm 15\%$.

With our experimental conditions and in the laboratory frame, the input laser beam propagating along the Z -axis is polarized along the X -axis and the measured macroscopic β_c^2 valid for all the molecular symmetry is given by

$$\beta_c^2 = \beta_{XXX}^2 + \beta_{ZXX}^2, \quad (2)$$

where

$$\beta_{XXX}^2 = \frac{1}{7} \sum_i \beta_{iii} + \frac{6}{35} \sum_{i,j} \beta_{iii} \beta_{ijj} + \frac{9}{35} \sum_i \beta_{ijj}^2 + \frac{6}{35} \sum_{i,j,k} \beta_{ijj} \beta_{ikk} + \frac{12}{35} \sum_i \beta_{ikj}^2,$$

$$\beta_{ZXX}^2 = \frac{1}{35} \sum_i \beta_{iii} - \frac{2}{105} \sum_{i,j} \beta_{iii} \beta_{ijj} - \frac{11}{105} \sum_i \beta_{ijj}^2 - \frac{2}{105} \sum_{i,j,k} \beta_{ijj} \beta_{ikk} + \frac{8}{35} \sum_i \beta_{ikj}^2$$

and i, j, k are defined in the molecular frame along the molecular axis labeled hereafter x, y, z . Therefore our experimental measurements only give access to two independent coefficients $\beta_{XXX}^2, \beta_{ZXX}^2$. Clearly, without simplifications about the molecular symmetry, it is almost impossible to deduce molecular hyperpolarizability $\beta_{ijk}^{(2)}$ from hyper-Rayleigh measurements. For instance, for molecules belonging to the C_2 group of symmetry, they are four independent $\beta^{(2)}$ (i.e., $\beta_{yyy}^{(2)}, \beta_{xyx}^{(2)}, \beta_{zzy}^{(2)}, \beta_{yxx}^{(2)}$) coefficients. Therefore unless some simplifications about the molecular symmetry are made, no useful information can be deduced from HRS experiments. For instance, the situation is greatly simplified, if one considers the molecule as planar, therefore belonging to C_{2v} group of symmetry, where only the $\beta_{xxx}^{(2)}, \beta_{xyy}^{(2)}$ coefficient remain. Further simplification is obtained for molecules belonging

to D_{3h} group symmetry since $\beta_{xxx}^{(2)} = -\beta_{xyy}^{(2)}$. For C_{2v} and D_{3h} molecules, the macroscopic hyperpolarizability is given by Eqs. (3) and (4), respectively,

$$\beta_c^2 = \beta_{xyy}^2 (31(1 + \beta_{xxx}/\beta_{xyy})^2/210 + 4(3 - \beta_{xxx}/\beta_{xyy})^2/210), \quad (3)$$

$$\beta_c^2 = 32\beta_{xxx}^2/105. \quad (4)$$

Such equation can be further extended to C_2 and D_3 molecules if β'_z components remain negligible in regard to the others β in-plane components. While such may look crude it has been proposed and justified for analyzing crystal violet analogous, known to belong to D_3 and C_2 group symmetries [26].

3. Results and discussion

Molecular nonlinear coefficients of compounds **1–8** were determined in CH_2Cl_2 solution at room temperature using HLS experiments. Fig. 1 shows a typical concentration dependence of the ratio $I_{2\omega}/(I_\omega^0)^2$ for this series of compounds. The curvature in the plots implies the intensity attenuation due to the absorption of the frequency doubled light. Fortunately, the absorption cross-section recorded at 532 nm is low (Table 1) and therefore

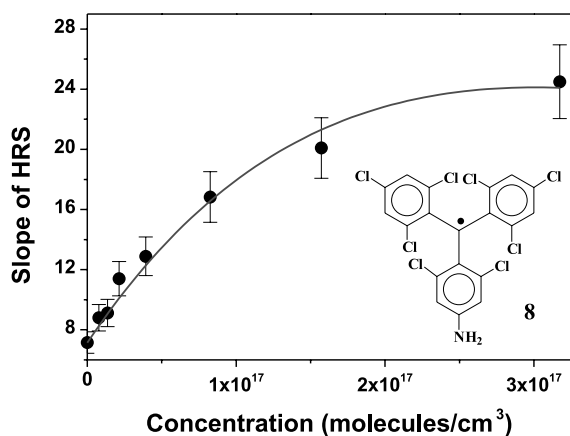


Fig. 1. Plot of hyper-Rayleigh scattering intensity versus the number density of radicals **8** in CH_2Cl_2 at room temperature. The curves in solid line represent the theoretical fit to equation (see text) obtained from the experimental data points.

the accuracy of the β value remains good for all the investigated compounds. The β values are calculated from the slope of the curve at the origin. The macroscopic value β_c of all the compounds (Table 1) were calibrated against CH_2Cl_2 ($\beta_s \approx 0.43 \times 10^{-30}$ esu), used as solvent.

Data reported in Table 1 show that the polychlorotriphenylmethyl radicals **1–8** exhibit very high SONLO response. In first view, it is not surprising since this family of radicals is structurally very similar to the octupolar symmetry of crystal violet, which exhibit a large β value [27–30]. In fact, both types of compounds have the general formulae $Ar^1Ar^2Ar^3Z$, where Z is an sp^2 hybridized atom – a C^+ in crystal violet and C in triphenylmethyl radicals – and Ar^i denotes an aromatic group. The polychlorotriphenylmethyl radicals **1–8** constitute a very attractive open-shell series that combines both a high NLO response and a good chemical, thermal, and photo-optical stabilities.

If we look more in detail the polychlorotriphenylmethyl radicals family it is interesting to note that **1–8** compounds belong to two different groups of symmetry. The symmetry of the studied radicals are either D_3 (**1,5,6**) or C_2 (**2–4** and **7–8**), assuming for some of the latter radicals that the substituents at the *para* position have time-averaged spherical shapes. The previous reported X-ray crystal structures of radicals **1,2,4–6** showed that the central C atom, bonded to the three phenyl rings, lies in the plane defined by the three bridging aromatic C atoms according with its sp^2 hybridization [18–23]. Moreover, the bulky Cl atoms in *ortho* positions induce a torsion of the phenyl rings around the bonds connecting with the central C atom with the same twist sense for the three rings so that the molecules adopt an helical arrangement.

From a symmetry point of view, a compound with a C_2 group of symmetry has a permanent dipole moment. The combination of both high β_c values and permanent dipole moment, as observed for **2–4** and **7–8** octupolar compounds, is very promising for designing molecular material with SONLO response at the macroscopic scale induced by poling technique with a static electric field. Obviously, the magnitude of the β_c values listed

for compounds 2–4 and 7–8 is strongly affected by the nature of the octupolar molecule. Independently, to the absorption cross-section and fluorescence, molecular hyperpolarizabilities are ranged between 118×10^{-30} esu (3) and 593×10^{-30} esu (7). This points out that the choice of the molecular arrangement with octupolar component is particularly important for further optimizing both the magnitude of the β_c value and the presence of a permanent dipole moment. As we pointed out previously, according to the data recorded with the HLS experiments, it is difficult to expect to optimize the NLO properties of molecules belonging to a C_2 group of symmetry since four independent coefficients contribute to the β_c value. Let us then reduce our approach to the simplest geometry; i.e., the planar one.

From a symmetry point of view, permanent dipole moment in planar geometry can be achieved by lowering the octupolar symmetry from D_{3h} to C_{2v} . In this latter symmetry, permanent ground state dipole moment can be oriented along the C_2 axis. Under our experimental HLS conditions [24,25], the expression β_c^2 of D_{3h} molecules only depends on β_{xxx}^2 (Eq. (4)) and of C_{2v} molecules on two molecular β_{xxx} and β_{xyy} components (Eq. (3)). Therefore, the case of C_{2v} molecules is more complex. With constant β_{xyy} , the β_c^2 is predicted to either increase or decrease depending on the sign and the amplitude of the β_{xxx}/β_{xyy} ratio (Fig. 2). Let us consider the 1,3,5-trichlorobenzene (TCB) and the pentachlorobenzene (PCB) compounds as example. Both of them have an octupolar component and belong, respectively, to D_{3h} and C_{2v} group of symmetry. Experimental HLS measurements show that the macroscopic molecular hyperpolarizability of TCB ($\beta_c = 22 \times 10^{-30}$ esu) is higher than of PCB ($\beta_c = 8 \times 10^{-30}$ esu). This behavior can be qualitatively understood according to Fig. 2, by placing the x -axis along the H-phenyl-Cl axis and the z -direction perpendicular to the phenyl ring of the octupolar molecule. TCB belongs to D_{3h} group symmetry and the ratio β_{xxx}/β_{xyy} is equal to -1 while for PCB with C_{2v} group the β_c^2/β_{xyy}^2 is directly dependent of the ratio β_{xxx}/β_{xyy} . From TCB to PCB, electronic modifications are very small and then the β_{xxx}/β_{xyy} factor should remain negative. Moreover, it can be considered

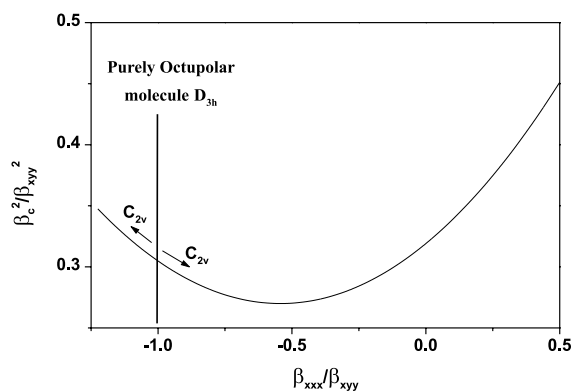


Fig. 2. Relation between the macroscopic β_c^2 and the two molecular β_{xxx} , β_{xyy} components for planar molecule belonging either to C_{2v} and D_{3h} symmetry groups. In our experimental HLS conditions, the β_{xxx}/β_{xyy} ratio of purely octupolar compound (D_{3h} symmetry group) is equal to -1 .

that the β_{xxx} increases more slightly than the β_{xyy} from TCB to PCB, as the increase number of Cl groups favors the electronic delocalization along the Y -axis. Consequently, according to Fig. 2, the negative β_{xxx}/β_{xyy} ratio is predicted to decrease from TCB (D_{3h}) to PCB (C_{2v}) and the β_c^2/β_{xyy}^2 should decrease, as experimentally observed.

The relationship between β_c^2/β_{xyy}^2 and β_{xxx}/β_{xyy} (Fig. 2) appears then particularly useful to further design octupolar molecules with high SONLO molecular properties and permanent ground state dipole moments. The main condition for octupolar molecules is that they should have vanishing molecular components, such as β_{zyy} and β_{zzz} , along a unique Z -axis. Basically, this condition is fulfilled for a planar configuration where the contribution of molecular components, such as β_{zyy} with the Z -axis perpendicular to the molecular plane, can be neglected. But this situation also occurs for other octupolar molecules having a three-bladed propeller conformation where each blade has a local C_2 symmetry and which show either a D_3 or C_2 symmetry. The β tensor element with the z element, such as β_{zzz} , are not strictly zero for D_3 or C_2 symmetry but these components can be neglected in comparison to the others β in-plane components (β_{yyy} , β_{xxx} , etc.) [26]. This hypothesis seems to be also realistic for the polychlorinated triphenylmethyl radicals family. The X-ray data

have revealed that the z -contribution linked to the helical arrangement induced by the torsion angle of the phenyl rings around the bonds connecting with the central C remained modest in regard to the x, y -contributions [18–23].

According to Fig. 2, the β_c^2 of a C_{2v} (or C_2) molecules with constant β_{xyy} is predicted to either increase or decrease depending on the sign and the amplitude of the β_{xxx}/β_{xyy} ratio. In Table 1, the optical properties of studied radicals are presented. It is interesting to compare such properties gathering the compounds in two series. One series, radicals **1–4**, containing two (or three) octupolar building blocks derived from PCB, while the other series, radicals **6–8**, have two (or three) of such blocks derived from TCB. Concerning the first series, the experimental β_c value of the purely octupolar compound **1** (362×10^{-30} esu) is similar to **2**, larger than **3** (118×10^{-30} esu) and lower than **4** (407×10^{-30} esu). This well confirms that for a series of C_2 molecules the β_c value may also either decrease or increase, as predicted by Fig. 2. The increase of β_c for **4** versus **1** is particularly interesting, as the former compound combines both a large SONLO signal and a permanent dipole moment. The study of compounds PCB and TCB has already showed that the β_{xyy} contribution decreases from PCB to TCB. Therefore in regard to the octupolar compound **1** (D_3 , $\beta_{xxx}/\beta_{xyy} = -1$) compound **4** is expected to possess a $\beta_{xxx}/\beta_{xyy} < -1$ and according to Fig. 2 this perfectly explains the increase of the β_c value assuming that other components remain constant. Note that this argument holds since we neglect the z tensor elements such as β_{zzz} . Similar argument allows understanding the β_c decrease from radicals **6** to **7**.

From all these examples, it is now clear that the model proposed in Fig. 2 can be useful to further optimize compounds belonging to D_{3h} and C_{2v} symmetries and also D_3 and C_2 symmetry if the z components remain negligible. Starting from D_{3h} (or D_3) symmetry ($\beta_{xxx}/\beta_{xyy} = -1$) increases of the β_c value can be obtained by rising the β_{xxx} component or by lowering the β_{xyy} component. Further chemical modifications of the radicals with donor–acceptor substituents are currently in progress.

Let us now examine if synergetic effect can be observed for a given symmetry between an indi-

vidual pure octupolar molecule and a ‘super-octupolar’ systems constituted itself with individual octupolar blocks. The study of the polychlorinated triphenylmethyl radicals gives access to such ‘super-octupolar’ systems. Indeed, each radical compounds **1–8** are composed of three individual building blocks having an octupolar contribution and the whole molecule has also a global octupolar contribution. Along this line, the comparison between purely octupolar radical compounds **1** and **6** is very interesting.

Both systems have a D_3 symmetry and according to the model of Fig. 2 compounds **1** and **6** remain in the $\beta_{xxx}/\beta_{xyy} = -1$ situation. They are composed of three individual building blocks with octupolar contributions based on PCB and TCB, respectively. HLS measurements show that the β_c value of **1** (362×10^{-30} esu) is lower than of **6** (755×10^{-30} esu). Interestingly, these experimental data follow the trend of the molecular hyperpolarizabilities derived from each individual octupolar blocks; i.e., PCB (8×10^{-30} esu) and TCB (22×10^{-30} esu), suggesting that a synergetic effect between individual building blocks may occur. Nevertheless, the absorption of PCB and TCB are so different than the analogous compounds **1** and **6** that due to potential resonant enhancement effect any significant conclusion about the ‘super-octupolar’ nature of the polychlorotriphenylmethyl radicals remains uncertain. Further works along this idea are currently in progress.

4. Conclusion

We showed for the first time that the polychlorotriphenylmethyl radicals **1–8** constitute a very attractive open-shell series that combines both a high NLO response and good chemical, thermal, and photo-optical stabilities. We also demonstrated that some compounds belonging to C_2 symmetry group exhibit high SONLO value. Variation between compounds has been interpreted according to the model proposed in Fig. 2. Finally, we suggested that a synergetic effect between octupolar blocks leading to the formation of a ‘super-octupolar’ system may occur. Others compounds belonging to D_3 symmetry are cur-

rently prepared to further understand this synergetic phenomenon. This approach is important for organizing independent octupolar molecules at a macroscopic scale.

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